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⑮ CANADIAN PATENT

⑯ PROCESS FOR PREPARING POLYARYLENE POLYETHERS

Robert A. Clendinning, New Providence, New Jersey, U. S. A.
Alford G. Farnham, Mendham, New Jersey, U. S. A.,
Nathan Zutty, Westfield, New Jersey, U. S. A., and
David C. Priest, Scott Depot, West Virginia, U. S. A.

Granted to Union Carbide Corporation, New York, New York,
U. S. A.

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This invention relates to improved one-step and two-step processes for the preparation of substantially linear, thermoplastic polyarylene polyethers.

PRIOR ART

In U.S. Patent 3,264,536, issued August 2, 1966, there are described one-step and two-step processes for the preparation of linear thermoplastic polyarylene polyethers composed of recurring units having the formula

-O-E-O-E'-

10 wherein E is the residuum of a dihydric phenol and E' is the residuum of a dihalobenzoid compound having an inert electron withdrawing group in at least one of the positions ortho and para to the valence bonds, and where both of said residua are covalently bonded to the ether oxygens through aromatic carbon atoms. In the one-step process for preparing these polymers, substantially equimolar amounts of an alkali metal double salt of a dihydric phenol and a dihalobenzoid compound having an inert electron withdrawing group as described above are reacted in the presence of specific liquid organic sulfoxide or sulfone reaction solvents 20 under substantially anhydrous conditions. In the two-step process, a dihydric phenol is first converted in situ in the sulfoxide or sulfone reaction solvent to the alkali metal salt by reacting with an alkali metal hydroxide. Thereafter, water which is present or formed is removed to secure substantially anhydrous conditions, and thus formed alkali metal double salt of a dihydric phenol is reacted with about stoichiometric amounts of a dihalobenzoid compound which is added in the in situ conversion.

As indicated above, anhydrous conditions must be maintained during the reaction otherwise if water is present in the reaction mass,

the unreacted dihalobenzoid compound becomes hydrolyzed leading to the formation of phenolic species and undesirable low molecular weight products. Water can be present or formed in the reaction mass as the water of hydration of the hydrated alkali metal double salt which if not removed will be liberated during the polymerization reaction or as the water of neutralization formed during the in situ conversion of a dihydric phenol to the alkali metal salt. Thus, it can be seen that the monovalent alkali metal hydroxide is the reason why water is present or formed in the reaction mass and this water must be removed, usually by azeotropic distillation, to secure substantially anhydrous conditions which means not more than about one per cent by weight water and preferably less than 0.5 per cent water by weight in the reaction mass.

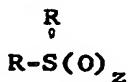
SUMMARY

It has now been found that thermoplastic polyarylene polyethers of the type described herein can be prepared by an improved process which comprises simultaneously contacting, under substantially anhydrous conditions, equimolar amounts of a dihydric phenol and a dihalobenzoid compound having an inert electron withdrawing group in at least one of the positions ortho and para to the halogen atoms, and at least one mole of an alkali metal carbonate per mole of dihydric phenol in the liquid phase of a sulfoxide or sulfone reaction solvent reacting the dihydric phenol with the alkali metal carbonate to form the alkali metal salt thereof and reacting the thus formed salt with the dihalobenzoid compound to form the polyarylene polyether.

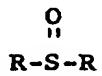
Because the present invention involves the reaction of a dihydric phenol and a divalent alkali metal carbonate, the by-product of this reaction is the alkali metal bicarbonate rather than water as is the case when monovalent alkali metal hydroxides are employed.

DESCRIPTION

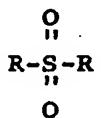
The polymerization reaction proceeds without the need of a catalyst, but the use of specific sulfoxide or sulfone reaction solvents is essential to promote the reaction to a useful, high molecular weight product. The sulfoxide or sulfone reaction solvents are those having the following generic formula



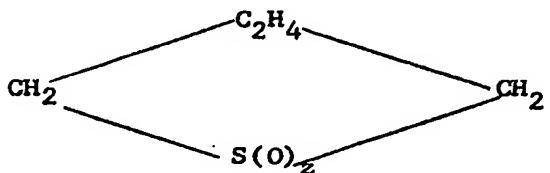
where each R represents a monovalent lower hydrocarbon group free of aliphatic unsaturation on the alpha carbon atoms, and preferably contains less than about 8 carbon atoms or when connected together represents a divalent alkylene group with z being an integer from 1 to 2 inclusive. Thus, in all of these solvents all oxygens and two carbon atoms are bonded directly to the sulfur atom. Thus, contemplated for use in this invention are such solvents as those having the formula



and



where the R groups are lower alkyl, such as methyl, ethyl, propyl, butyl and like groups and aryl groups such as phenyl and alkyl phenyl groups as well as those where the R groups are interconnected as in a divalent alkylene bridge such as



as in thiophene oxides and dioxides. Suitable solvents include dimethylsulfoxide, dimethylsulfone, diethylsulfoxide, diethylsulfone, diisopropylsulfone, diphenylsulfone, tetrahydrothiophene 1,1-dioxide (commonly called tetramethylene sulfone or sulfolane), tetrahydrothiophene-1 monoxide and the like. Sulfolane has been found to be the most useful as the solvent for this reaction because it is a solvent for the widest variety of reactants as well as for the resulting polymer of the reaction. Aliphatic unsaturation on the α carbon atoms, such as occurs in divinyl sulfone and sulfoxide, should not be present as such materials tend to be reactive and polymerize under the conditions of this reaction. However, unsaturation of a β carbon atom or one further removed from the sulfur atoms can be tolerated and such solvents can be employed in this reaction.

As indicated previously, the dihydric phenol, dihalobenzoid compound and anhydrous alkali metal carbonate are all present in the reaction mass at once. The carbonate is thought to react with one of the aromatic hydroxyl groups of the phenol producing the monoalkali metal salt of the phenol and the bicarbonate of the alkali metal. The carbonate can also react with both hydroxyl groups to form the di-salt but it is thought that the formation of the mono-salt predominates. These mono- and di- salts are then capable of entering into the polymerization reaction with the dihalobenzoid compound present in the reaction mass. The reaction between a mono- salt and a dihalobenzoid compound produces a compound comprising the two monomers joined by an aromatic ether linkage and having a hydroxyl group and a halogen group at either ends of the compound molecule. The aromatic hydroxyl group of this compound then reacts with the alkali metal carbonate in the reaction mass producing the

alkali metal salt which then reacts with dihalobenzoid compound to lengthen the polymer chain, and so on. With the di-salt, there is no two-stage formation of the salt and polymerization proceeds smoothly. However the two-stage formation as discussed above is believed to be the predominate polymer forming reaction.

Under the conditions of the in situ conversion of the aromatic hydroxyl groups to the alkali metal salt and the polymerization reaction it has been found that certain of the alkali metal bicarbonates that are formed during the in situ conversion are unstable and 2 moles decompose into 1 mole of carbon dioxide, 1 mole of the corresponding alkali metal carbonate and 1 mole of water. The alkali metal carbonate formed as a result of the bicarbonate decomposition can then react with aromatic hydroxyl groups present in the reaction mass. Potassium bicarbonate decomposes over the range of 100-200°C. and rubidium and cesium bicarbonate decompose at 175°C. Sodium bicarbonate is somewhat more stable but does decompose in the manner indicated. Lithium bicarbonate does not decompose under any conditions. For purposes of this invention, it is preferred, therefore, to employ sodium or potassium carbonate since rubidium and cesium carbonate are comparatively expensive and lithium carbonate is a slow reactor.

From the foregoing, it can be seen that from one of the two moles of alkali metal carbonate can be used for the in situ conversion of each mole of dihydric phenol. In the case of the halophenol described herein containing one aromatic hydroxy group, from one-half to one mole of alkali metal carbonate is used for each mole of halophenol. Since it is thought that the predominate reaction is the two-stage neutralization of the aromatic hydroxyl groups, the use of one mole of alkali metal carbonate or a slight excess (e.g., 1 to 10 per cent in excess of one mole) for each mole of the dihydric phenol is more economical although up to two moles of alkali metal carbonate for each mole of dihydric phenol can be used if desired.

Thus, in the predominate reaction between a mono- salt and the dihalobenzoid compound discussed above, the second aromatic hydroxyl group is converted in the second stage to the alkali metal salt by reaction with alkali metal carbonate formed in the reaction mass by the decomposition of unstable bicarbonate. Apparently, because the polymerization reaction is well under way before water is formed during the decomposition of the alkali metal bicarbonate, its removal from the reaction mass is not necessary to produce a polymer, but it
10 is preferred in order to insure the formation of high molecular weight polymer. Water which is formed in the reaction mass in the foregoing manner can be tolerated in amounts in excess of one per cent by weight, but preferably the system is maintained substantially anhydrous, that is, less than one per cent, and preferably less than one-half per cent, by weight water in the reaction mass.

It is preferred that the reactants and solvents charged to the reaction mass be substantially anhydrous. If any of these are not sufficiently dry, they can be rendered so prior to reaction by suitable means such as by using an azeotrope former as described herein. For the in situ conversion of the dihydric phenol to the alkali metal salt, it is preferred to start with anhydrous dehydrated alkali metal carbonate. However, if the hydrated form is used, it can be dehydrated in the reaction mass as described herein.
20

In order to maintain substantially anhydrous conditions, water that is present or formed in the reaction mass is removed as an azeotrope with an azeotrope former. It should be noted that any of the initial reactants and/or reaction solvent can be rendered substantially anhydrous in this manner before contacting all of the
30

initial reactants. It has been found convenient to employ benzene, xylene, halogenated benzenes or other inert organic azeotrope-forming organic liquids in performing this. Water is removed by heating at reflux and removing the azeotrope that is formed.

It is not essential that all of the azeotrope former be removed. In fact, it is desirable to employ an amount of such material in excess of that needed to azeotrope off the water, with the balance being used as a cosolvent or inert diluent with the sulfone or sulfoxide reaction solvent. Thus, for instance, benzene, heptane, xylene, toluene, chlorobenzene, dichlorobenzene, and the like inert liquids can be beneficially employed.

10 The azeotrope former can be one either miscible or immiscible with the sulfone or sulfoxide reaction solvent. If it is not miscible it should be one which will not cause precipitation of the polymer in the reaction mass. Heptane is such a solvent. When employed, it will merely remain inert and immiscible in the reaction mass.

It is preferred to employ azeotrope formers which are miscible with the major solvents and which also act as cosolvents for the polymer during polymerization. Chlorobenzene, dichlorobenzene and xylene are azeotrope formers of this class. Preferably the azeotrope former should be one boiling below the decomposition temperature of the major solvent and be perfectly stable and inert in the process, particularly inert to the alkali metal carbonate.

It has been found that chlorobenzene and o-dichlorobenzene serve particularly well as the inert diluent and are able to significantly reduce the amount of the sulfone or sulfoxide reaction solvent necessary. The cosolvent mixture using even as much as 50 per cent by weight of the halogenated benzene with dimethylsulfoxide 20 for example, not only permits the formed polymer to remain in solution and thus produce high molecular weight polymers, but also provides a very economical processing system. These materials are also completely stable to the alkali metal carbonates.

The reaction between the dihalobenzoid compound and the alkali metal salt of the dihydric phenol proceeds essentially on an equimolar basis. This can be slightly varied but as little as a variation as 5 per cent away from equal molar amounts seriously reduces the molecular weight of the polymers. Thus, essentially equal molar amounts are preferred.

The in situ conversion and polymerization reaction readily proceed without need of an added catalyst upon the application of heat to such a mixture in the selected sulfone or sulfoxide solvent.

10 Inasmuch as the in situ conversion and polymerization reaction are conducted in the liquid phase of the solvent, the selected reaction temperature should be below the ambient boiling point of solvent and above its freezing point. Thus, such solvents are tetramethylene sulfone (sulfolane) that freeze at about room temperatures require elevated temperatures.

20 While the reaction temperature is not narrowly critical, it has been found that at temperatures below about room temperature, the reaction time is inordinately long in order to secure high molecular weight polymers. The higher temperatures i.e. above room temperature and generally about 100°C., are much more preferred for shorter processing times and for a more economical system. Most preferred are temperatures between about 120°C. to 240°C. Higher temperatures can of course be employed, if desired, provided that care is taken to prevent degradation or decomposition (other than the unstable bicarbonates) of the reactants, the polymer and the solvents employed.

30 Temperatures higher than 100°C. are preferred in order to keep the polymer in solution during the reaction since the sulfoxide and sulfone solvents are not particularly good solvents for the polymer except in the hot condition. High molecular weights are possible only

when the growing polymer chain is dissolved in the solvent. Once the polymer precipitates from the solvent, its growing ceases, although it has been found that when this happens, the addition of a second cosolvent as hereinbefore mentioned to the reaction or by increasing the reaction temperature, the precipitated polymer can be resolivated and the polymerization continued to higher molecular weights. Among such other cosolvents as might be mentioned for use solely to increase the fluidity of the reaction mass are diphenyl ether, anisole, xylene, chlorobenzene or dichlorobenzene and like 10 materials even though other azeotrope formers may have previously been used or are still in the reaction mass.

The reaction temperature can be effectively increased even above the normal boiling point of the solvent or mixture of solvents by the use of pressure in the system. However, for most practical reactions contemplated herein, atmospheric pressures are quite adequate, though if desired pressures as high as 1000 psig. or more can be employed.

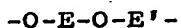
Preferably the monomer reactants are in a solution at the reaction temperature. However, the reaction can still proceed 20 as a swollen gel of solvent and dissolved polymer if high solids reaction conditions are desired. This of course depends on the amount of reaction solvent initially present and on the power of the agitator in the vessel. Desirably, it has been found that equal parts by weight of reaction solvent and of total monomer reactants (based on the weight of sulfoxide or sulfone reaction solvent, exclusive of the azeotrope former, and total monomer reactants) seem to give optimum results. However, if adequate stirring is provided and means are available for stripping the solvent from the polymer mass are provided, as little as one part 30 reaction solvent to five or more parts total monomer reactants can be used.

The polymer is recovered from the reaction mass in any convenient manner, such as by precipitation induced by cooling the reaction mass or by adding a nonsolvent for the polymer, or the solid polymer can be recovered by stripping off the solvent at reduced pressures or elevated temperatures.

Molecular weight of the polymer can be easily controlled by the addition of a precipitating solvent to the reaction mixture when the desired reduced viscosity of the resin is secured or when the indicated viscosity of the polymerization mass is high enough 10 to indicate the desired molecular weights are achieved. It is also possible to terminate the growing polymer chain by the addition of a monofunctional chain stopper, such as an alkyl halide or other suitable coreactant.

Since the polymerization reaction results in the formation of the alkali metal halide on each coupling reaction, it is preferred to either filter the salts from the polymer solution or to wash the polymer to substantially free it from these salts. For such reasons, the precipitation of the polymer from the reaction mass as a fluffy powder or fine granule is preferred, although chain termination is 20 also beneficial in yielding a more stable polymer.

As stated previously, thermoplastic polyarylene polyethers prepared herein have a basic structure composed of recurring units having the formula



wherein E is the residuum of a dihydric phenol and E' is the residuum of a benzenoid compound having an inert electron withdrawing group in at least one of the positions ortho and para to the valence bonds, and where both of said residua are valently bonded to the ether oxygens through aromatic carbon atoms.

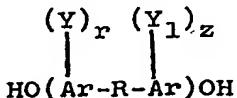
30 The residuum E of the dihydric phenol can be, for instance, a mononuclear phenylene group as results from hydroquinone and resorcinol, or it may be a di- or polynuclear residuum. The residuum

E can also be substituted with other inert nuclear substituents such as halogen, alkyl, alkoxy and like inert substituents.

It is preferred that the dihydric phenol be a weakly acidic dinuclear phenol such as, for example, the dihydroxy diphenyl alkanes or the nuclear halogenated derivatives thereof, which are commonly known as "bisphenols," such as, for example, the 2,2-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)-2-phenyl ethane, bis(4-hydroxyphenyl)methane, or the chlorinated derivatives containing one or two chlorines on each aromatic ring.

10 Other suitable dinuclear dihydric phenols are the bisphenols of a symmetrical or unsymmetrical joining group as, for example, either oxygen (-O-), carbonxyl (-CO-), sulfide (-S-), sulfone (SO_2-), or hydrocarbon residue in which the two phenolic nuclei are joined to the same or different carbon atoms of the residue such as, for example, the bisphenol or acetophenone, the bisphenol of benzophenone, the bisphenol of vinyl cyclohexene, the bisphenol of α -pinene, and the like bisphenols where the hydroxyphenyl groups are bound to the same or different carbon atoms of an organic linking group.

20 Such dinuclear phenols can be characterized as having the structure:



wherein Ar is an aromatic group and preferably is a phenylene group, Y and Y_1 can be the same or different inert substituent groups as alkyl groups having from 1 to 4 carbon atoms, halogen atoms, i.e. fluorine, chlorine, bromine, or iodine, or alkoxy radicals having from 1 to 4 carbon atoms, r and z are integers having a value of from 0 to 4 inclusive, and R is representative of a bond between aromatic carbon atoms as in dihydroxydiphenyl, or is a divalent radical, including for example, inorganic radicals as

-CO-, -O-, -S-, -S-S-, -SO₂-, and divalent organic hydrocarbon radicals such as alkylene, alkylidene, cycloaliphatic or the halogen, alkyl, aryl or like substituted alkylene, alkylidene and cycloaliphatic radicals as well as alkalicyclic, alkarylene and aromatic radicals and a ring fused to both Ar groups.

- Examples of specific dihydric polynuclear phenols include among others: the bis-(hydroxyphenyl)alkanes such as 2,2-bis-(4-hydroxyphenyl)propane, 2,4'-dihydroxydiphenylmethane; bis-(2-hydroxyphenyl)methane, bis-(4-hydroxyphenyl)methane, bis-(4-hydroxy-10 2,6-dimethyl-3-methoxyphenyl)methane, 1,1-bis(4-hydroxyphenyl)-ethane, 1,2-bis(4-hydroxyphenyl)ethane, 1,1-bis-(4-hydroxy-2-chlorophenyl)ethane, 1,1-bis-(3-methyl-4-hydroxyphenyl)propane, 1,3-bis-(3-methyl-4-hydroxyphenyl)propane, 2,2-bis-(3-phenyl-4-hydroxyphenyl)propane, 2,2-bis-(3-isopropyl-4-hydroxyphenyl)propane, 2,2-bis-(2-isopropyl-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxy-naphthyl)propane, 2,2-bis-(4-hydroxyphenyl)pentane, 3,3-bis-(4-hydroxyphenyl)pentane, 2,2-bis-(4-hydroxyphenyl)-1-phenylpropane, 2,2-bis-(4-hydroxyphenyl)-1,1,1, 3,3,3-hexafluoropropane and the like;
- 20 di(hydroxyphenyl)sulfones such as bis-(4-hydroxyphenyl)-sulfone, 2,4'-dihydroxydiphenyl sulfone, 5'-chloro-2,4'-dihydroxy-diphenyl sulfone, 5'-chloro-4,4'-dihydroxydiphenyl sulfone, and the like; the bisphenols of cyclohexanone, norcamphor and the like; di(hydroxyphenyl)ethers such as bis-(4-hydroxyphenyl)ether, the 4,3'-, 4,2'-, 2,2'-, 2,3'-dihydroxydiphenyl ethers, 4,4'-di-hydroxy-2,6-dimethyldiphenyl ether, bis-(4-hydroxy-3-isobutylphenyl)-ether, bis-(4-hydroxy-3-isopropylphenyl)ether, bis-(4-hydroxy-3-chlorophenyl)ether, bis-(4-hydroxy-3-fluorophenyl)ether, bis-(4-hydroxy-3-bromophenyl)ether, bis-(4-hydroxynaphthyl)ether, bis-(4-hydroxy-3-chloronaphthyl)ether, 4,4'-dihydroxy-3,6-dimethoxydiphenyl ether, 4,4'-dihydroxy-2,5-diethoxydiphenyl ether, and like materials.

It is also contemplated to use a mixture of two or more different dihydric phenols to accomplish the same ends as above.

Thus when referred to above the E residuum in the polymer structure can actually be the same or different aromatic residua.

As used herein, the E term defined as being the "residuum of the dihydric phenol" refers to the residue of the dihydric phenol after the removal of the two aromatic hydroxyl groups. Thus it is readily seen that polyarylene polyethers contain recurring groups of the residuum of the dihydric phenol and the residuum of the benzenoid compound bonded through aromatic ether oxygen atoms.

The residuum E' of the benzenoid compound can be from 10 any dihalobzenoid compound or mixture of dihalobzenoid compounds which compound or compounds have the two halogens bonded to benzene rings having an electron withdrawing group in at least one of the positions ortho and para to the halogen group. The dihalobzenoid compound can be either mononuclear where the halogens are attached to the same benzenoid ring or polynuclear where they are attached to different benzenoid rings, as long as there is the activating electron withdrawing group in the ortho or para position of that benzenoid nucleus.

Any of the halogens may be of the reactive halogen substituents on the benzenoid compounds, fluorine and chlorine substituted benzenoid reactants being preferred. 20

Any electron withdrawing group can be employed as the activator group in the dihalobzenoid compounds. Preferred are the strong activating groups such as the sulfone group (-SO₂-) bonding two halogen substituted benzenoid nuclei as in the 4,4'-dichlorodiphenyl sulfone and 4,4'-difluorodiphenyl sulfone, although such other strong withdrawing groups hereinafter mentioned can also be used with ease. It is further preferred that the ring contain no electron supplying groups on the same benzenoid nucleus as the 30 halogen; however, the presence of other groups on the nucleus or in the residuum of the compound can be tolerated. Preferably, all of the substituents on the benzenoid nucleus are either hydrogen (zero electron withdrawing), or other groups having a positive

sigma* value, as set forth in J.F. Bunnett in Chem. Rev., 49, 273 (1951) and Quart. Rev., 12, 1 (1958).

The electron withdrawing group of the dihalobzenoid compound can function either through the resonance of the aromatic ring, as indicated by those groups having a high sigma* value, i.e. above about +0.7 or by induction as in perfluoro compounds and like electron sinks.

Preferably the activating group should have a high sigma* value, preferably above 1.0, although sufficient activity is evidenced in those groups having a sigma* value above 0.7.

The activating group can be basically either of two types:

(a) monovalent groups that activate one or more halogens on the same ring as a nitro group, phenylsulfone, or alkylsulfone, cyano, trifluoromethyl, nitroso, and hetero nitrogen as in pyridine;

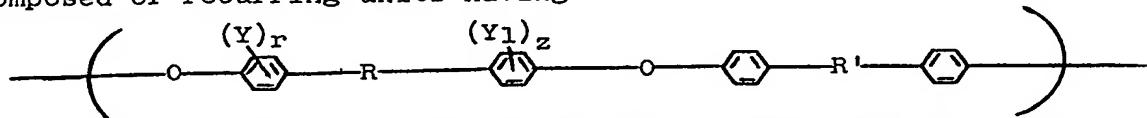
(b) divalent groups which can activate displacement of halogens on two different rings, such as the sulfone group $-\text{SO}_2-$; the carbonyl group $-\text{CO}-$; the vinyl group $-\text{CH}=\text{CH}-$; the sulfoxide group $-\text{SO}-$; the azo group $-\text{N}=\text{N}-$; the saturated fluorocarbon groups $-\text{CF}_2\text{CF}_2-$; organic phosphine oxides $-\overset{\text{R}}{\text{P}}-$; where R is a hydrocarbon

20 group, and the ethyldene group $\overset{\text{R}}{\text{C}}-\text{C}-$ where X can be hydrogen, or halogen or which can activate halogens on the same ring such as with difluorobenzoquinone, 1,4- or 1,5- or 1,8-difluoroanthraquinone.

If desired, the polymers may be made with mixtures of two or more dihalobzenoid compounds each of which has this structure, and which may have different electron withdrawing groups. Thus, the E' residuum of the benzenoid compounds in the polymer structure may be the same or different.

30 It is seen also that as used herein, the E' term defined as being the "residuum of the benzenoid compound" refers to the aromatic or benzenoid residue of the compound after the removal of the halogen atoms on the benzenoid nucleus.

From the foregoing, it is evident that preferred linear thermoplastic polyarylene polyethers are those wherein E is the residuum of a dinuclear dihydric phenol and E' is the residuum of a dinuclear benzenoid compound. These preferred polymers then are composed of recurring units having the formula



wherein R represents a member of the group consisting of a bond between aromatic carbon atoms and a divalent connecting radical

10 and R' represents a member of the group consisting of sulfone, carbonyl, vinyl, sulfoxide, azo, saturated fluorocarbon, organic phosphine oxide and ethylidene groups and Y and Y₁ each represent inert substituent groups selected from the group consisting of halogen, alkyl groups having from 1 to 4 carbon atoms and alkoxy groups having from 1 to 4 carbon atoms and where r and z are integers having a value from 0 to 4 inclusive. Even more preferred as the thermoplastic polyarylene polyethers of the above formula

wherein r and z are zero, R is divalent connecting radical $-C\begin{smallmatrix} R'' \\ | \\ R'' \end{smallmatrix}-$

20 wherein R'' represents a member of the group consisting of hydrogen, lower alkyl, lower aryl, and the halogen substituted groups thereof, and R' is a sulfone group.

Because the thermoplastic polyarylene polyethers prepared according to this invention have excellent physical, mechanical, chemical, electrical, and thermal properties, their uses are many and varied. For example, they can be used in molding formulations either along or mixed with various fillers and/or additives to make molded parts such as gears, ratchets, cams, impact parts, gaskets, valve seats and the like. They can be used to prepare 30 molded, calendered or extruded articles such as films, sheets, bars, rods, coatings, threads, filaments, tapes and the like.

They are useful in electrical applications such as in cable terminals, terminal blocks, diode sticks, wire and cable insulation, and the like. They can also be used as an encapsulation material for electrical insulation such as wire enamel, potting compound and the like. Their excellent electrical properties make laminates or sheets of these polymers useful for electrical equipment such as printed circuits, small appliance housings, slot wedges in the armature of an electrical motor, and the like.

The following examples are intended to further illustrate 10 the present invention without limiting the same in any manner.

Reduced viscosity (RV) is determined by dissolving a 0.2 gram sample of the polyarylene polyether in a selected solvent contained in a 100 ml volumetric flask so that the resultant solution measures exactly 100 ml at 25°C. in a constant temperature bath. The viscosity of 3 ml of the solution which has been filtered through a sintered glass funnel is determined in an Ostwald or similar type viscometer at 25°C. Reduced viscosity values are obtained from the equation:

$$\text{Reduced Viscosity} = \frac{t_s - t_o}{c \cdot t_o}$$

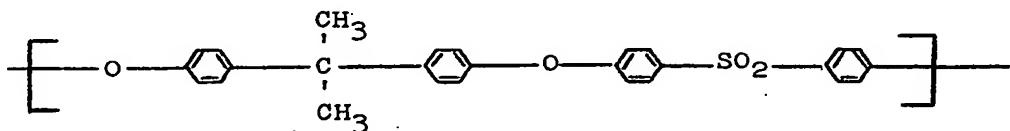
20 wherein: t_o is the efflux time of the pure solvent
 t_s is the efflux time of the polymer solution
 c is the concentration of the polymer solution
 expressed in terms of grams of polymer per
 100 ml of solution.

All parts and percentages are by weight unless indicated otherwise.

EXAMPLE 1

To a 4-necked flask; equipped with Dean Stark tube, stirrer, nitrogen sparge and thermometer, is charged 200 ml. 30 dimethylsulfoxide, 40 ml. toluene, 11.41 grams (0.05 moles) 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), 14.35 grams (0.05 moles) 4,4'-dichlorodiphenylsulfone and 13.82 grams (0.10 moles) anhydrous potassium carbonate. The mixture is heated to 150°C. and held at

149-152°C. for 7 hours. Small amounts of water are continuously removed by the toluene azeotrope. The viscous solution is cooled and filtered to remove salts. The polymer is isolated by addition of the filtrate to a large volume of methanol agitated in a Waring Blender. A quantitative yield of white polymer is filtered off and dried under vacuum. The product was a reduced viscosity of 0.46 (0.2 grams of polymer in 100 ml. chloroform at 25°C.) and is composed of recurring units having the formula:



A tough transparent plaque is molded from the polymer.

EXAMPLE 2

Using a procedure identical to Example 1, except that no toluene is added and no water of reaction is removed, there is obtained a quantitative yield of polymer having a reduced viscosity of 0.27 in chloroform. This example demonstrates that it is not necessary (though desirable) to remove water formed in the reaction mass.

20 EXAMPLE 3

In a 500 cc. 3-neck reaction flask fitted with a Y tube, thermometer, stirrer, nitrogen sparge tube, Dean Stark trap and condenser is placed.

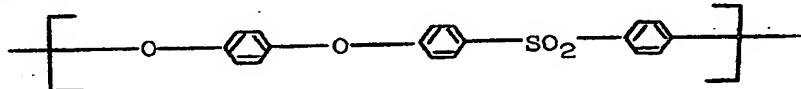
13.21 g. hydroquinone (0.12 mole),
100 cc. sulfolane, and
50 cc. toluene.

The mixture is heated to reflux and air is displaced by nitrogen.

The mixture is cooled to 100°C. and

30 34.46 g. 4,4'-Dichlorodiphenylsulfone (0.12 mole) and
20.7 g. K₂CO₃ (Granular anhydrous, 0.15 ground in mortar and oven dried at 220°) are added.

The mixture is heated to reflux at 133-4°C., a small amount of water (0.2 cc.) separated but there is no evidence that more would form on continued heating. Toluene is distilled out to raise the pot temperature to 210°C. Water collects to the extent of 1.8 cc. during 20-25 min. After reacting for 1 hour at 205-218°C. the mixture is very stiff. Methyl chloride is bubbled in, the mixture allowed to cool somewhat and diluted with chlorobenzene. The warm polymer solution is poured into a beaker and cooled to allow the polymer to crystallize. The crystallized product is washed in a 10 Waring blender with water and the filtered solid washed successively with hot alcohol and hot water. The finely granular polymer was vac. dried overnight at 150°C. The polymer has a reduced viscosity of 1.96 in p-chlorophenol at 47°C. and is composed of recurring units having the formula



EXAMPLE 4

This example is carried out as Example 3 except that chlorobenzene is used as the azeotrope solvent, a fractionating column is used below the trap and condenser, and the water-chlorobenzene is removed as distilled without returning it to the reaction 20 mixture. The reaction time is 3/4 hr. at 210-225°C. Yield is 38.1 g., R.V. 0.80 in p-chlorophenol at 47°C., Capillary M.P. 295-300°C. A film molded at 330° is clear and tough.

EXAMPLE 5

This experiment is carried out as Example 4 except that Na_2CO_3 (15.9 g. powder anhydrous) is used in place of K_2CO_3 and 20 cc. of chlorobenzene is added dropwise to the reaction mixture during the reaction period of 1 3/4 hr. at 230-236°C. The yield of polymer isolated and washed as in Example 3 is 38.1 g. (38.9 g. calc.) 30 and R.V. is 0.98 in p-chlorophenol at 47°C.

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EXAMPLE 6

The procedure of example 5 is repeated using 2-fold amount of reactants, except that K_2CO_3 (41.4 g.) was used instead of Na_2CO_3 . Reaction time is 55 min. at 210-220°C. Yield is 76.8 g. and R.V. 0.7: in p-chlorophenol at 47°C. The following properties are obtained for a molded film:

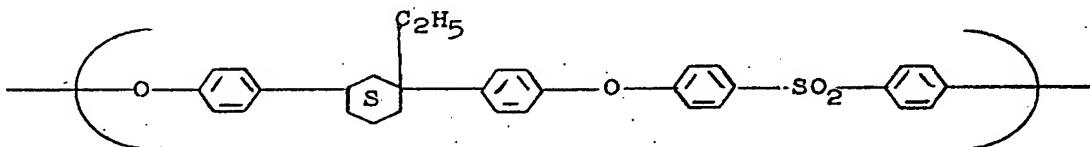
10	Tg	220°C.
	Tensile Modulus*	250,000 psi
	Yield Strength	9000 psi
	Yield Elongation	5.0%
	Ultimate Tensile Strength	9000 psi
	Ultimate Elongation	65-180%
	Pendulum Impact**	200-600 ft.lb/cu.in.

*Tensile Properties are determined according to ASTM D-638.

**Determined according to ASTM D-256-56.

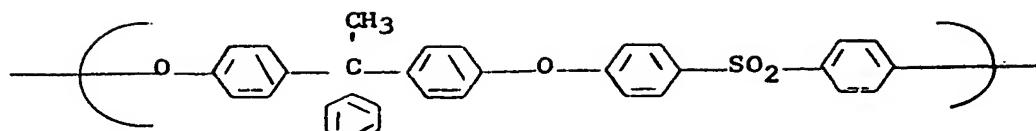
EXAMPLE 7

Example 1 is duplicated except that in place of bisphenol 39.1 grams (0.1314 mole) of 1,3-bis-(p-hydroxyphenyl)-1-ethylcyclohexane (the bisphenol prepared by an acid catalyzed condensation of 2 moles of phenol with one mole vinylcyclohexene is used. The isolated polymer has a light amber color and is composed of recurring units having the formula

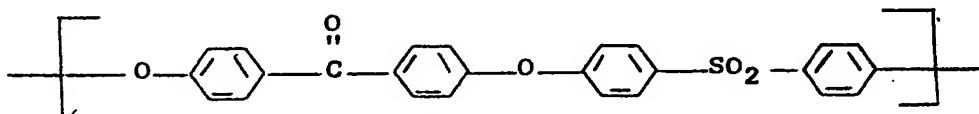


EXAMPLE 8

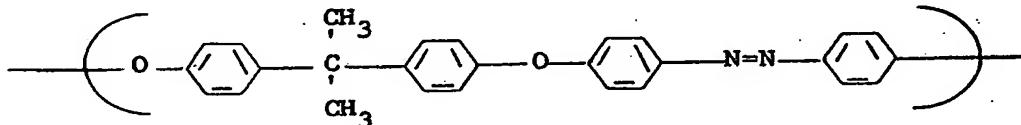
Example 1 is duplicated except that in place of bisphenol 38.2 grams (0.1314 mole) of 1,1-bis-(4-hydroxyphenyl)-1-phenylethane (bisphenol of acetophenone) is used. The isolated polymer has a light amber color and is composed of recurring units having the formula

EXAMPLE 9

Example 4 is duplicated except that in place of hydroquinone benzophenone is used. The isolated polymer is composed of recurring units having the formula

EXAMPLE 10

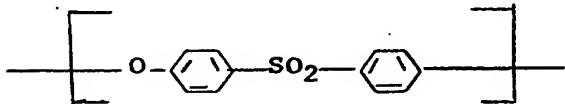
Example 4 was duplicated except that in place of 4,4'-dichlorodiphenylsulfone, 32.0 g. (0.1314 mole) of 4,4'-dichloroazobenzene is used. The isolated polymer has an orange color owing to the presence of the azo linkages and is composed of recurring units having the formula

EXAMPLE 11

To a 5 liter 4 necked flask fitted with a paddle stirrer, an argon inlet extending below the surface of the liquid two thermocouples (recording and controlling), an MCB trap, a reflux condenser connected to an argon bubbler, and an addition funnel is charged:

250.3 grams (1.0 mole) -4,4'-dihydroxydiphenyl sulfone
 287.2 grams (1.0 moles) -4,4'-dichlorodiphenyl sulfone
 165.2 grams (1.0 mole) potassium carbonate ($K_2CO_3 \cdot 1.5H_2O$)
 1890.0 grams (1500 ml.) Sulfolane($TMSO_2$)
 553.0 grams (500 ml.) Chlorobenzene (MCB)

The charge is heated to 235°C. removing distillate as the temperature increases. At 235°C. dropwise addition of MCB is started at such a rate that 717-770 gms (650-700 ml.) are added over a 90 min. period. The temperature is maintained at 235°C. for 6.5 hours, and the reaction terminated with methyl chloride. The terminated reaction is cooled to about 180-200°C. and 1216 g. (1290 ml) dimethylformamide (DMF) added. After cooling to room temperature, the reaction mixture is filtered and coagulated in 4 volumes of water. The coagulated polymer is then dried in a vacuum oven overnight at 50-70°C. to remove water and then put through a vented extruder to remove DMF and TiSO_2 . The isolated polymer has an RV of 0.81 in chloroform and is composed of recurring units having the formula



EXAMPLE 12

Example 11 is duplicated using 1 mole of sodium carbonate in place of potassium carbonate. The reaction time is 9 hours and the isolated polymer has an RV of 0.74 in chloroform.

20

EXAMPLE 13

Example 11 is duplicated using 99, 100, 101 and 120 mole percents of potassium carbonate to produce polymers having RV's of 0.45, 0.63, 0.76 and 70.35, respectively. This example demonstrates that for this particular polymer preparation (including the preparation of Example 14) the use of a slight excess (e.g. 1 to 10% molar excess) over one mole of alkali metal carbonate is desirable to produce high polymers but a greater excess (over 10%) leads to low molecular weight polymers composed

of recurring units having the formula

-O-D-

wherein E is the residuum of a halophenol having an electron withdrawing group ortho or para to the halogen atom which is valently bonded to the ether oxygen through aromatic carbon atoms as is more fully described below can also be prepared by employing the process of this invention. Polymers of this type exhibit excellent strength and toughness as well as outstanding thermal, oxidative and chemical stability. As such they find wide utility 10 in the production of shaped and molded articles, and in the preparation of film and fiber products.

Any halophenol can be employed in this invention which has the halogen and aromatic hydroxyl group bonded to benzene rings having an electron withdrawing group (as described herein) in at least one of the positions ortho and para to the halogen atom. The halophenol can be either mononuclear where the halogen and aromatic hydroxy group are attached to the same benzene ring or polynuclear where they are attached to different benzene rings, as long as there is the activating electron withdrawing 20 group in the ortho or para position of the benzene ring containing the halogen atom.

Any of the halogens may be the reactive halogen substituent on the halophenol. Fluorine and chlorine substituted halophenols are preferred; the fluorine compounds for fast reactivity and the chlorine compounds for their inexpensiveness.

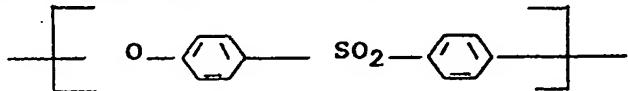
The halophenols described herein can be prepared using a conventional Friedel-Crafts procedure such as that described by Szmant et al in J.A.C.S., 78, 3400-03 (1956)

EXAMPLE 14

In a 500 ml. 4-necked flask equipped as in Example 1, were placed 26.88 g. (100 mmoles) of p-(p-chlorophenylsulfonyl)-phenol, 8.26 g. (50 mmoles) of hydrated potassium carbonate ($K_2CO_3 \cdot 1.5 H_2O$), 75 ml. of tetramethylene sulfone (sulfolane), and 50 ml. of chlorobenzene. The mixture was heated to 235°C., removing distillate as the temperature increased. At 235°C. 100 ml. of chlorobenzene was added over a period of 80 minutes, again removing distillate as it was formed. The reaction was continued at 235°C. for an additional 4 hours and 40 minutes giving a total reaction time at 235°C. of 6 hours.

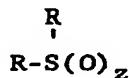
The polymerization was terminated by passing about 10 g. of methyl chloride through the reaction at 235°C. over a 15 minute period. After slight cooling, the polymer solution was diluted with 143 ml. of dimethylformamide and, when cooled to room temperature, filtered to remove insoluble salts. The polymer was coagulated in 4 volumes of water and the resultant powder dried in a vacuum oven at 150°C. and about 1 mm. Hg.

20 The powder weighed 19.8 g. (86% yield), had an R.V. of 0.60 (measured in N-methylpyrrolidone at 25°C., 0.05 g./ml.), and was composed of recurring units having the formula



WE CLAIM:

1. Process for preparing substantially linear, thermoplastic polyarylene polyethers which comprises simultaneously contacting, under substantially anhydrous conditions, substantially equimolar amounts of a dihydric phenol and a dihalobenzoid compound having an inert electron withdrawing group in at least one of the positions ortho and para to the halogen atoms with at least one mole alkali metal carbonate per mole of dihydric phenol in the liquid phase of an organic reaction solvent having the formula



where each R represents a member of the group consisting of monovalent lower hydrocarbon groups free of aliphatic unsaturation on the alpha carbon atom and, when connected together, represents a divalent alkylene group, and z is an integer from 1 to 2 inclusive, reacting said dihydric phenol with said alkali metal carbonate to form the alkali metal salt thereof, and the bicarbonate of said alkali metal, and reacting the thus formed alkali metal salt with said dihalobenzoid compound in the liquid phase of reaction solvent.

2. The process of claim 1 wherein the reaction is conducted at elevated temperatures.

3. The process of claim 1 wherein the reaction is conducted at a temperature above about 100°C. and below the decomposition temperature of the reactants, the reaction solvent, and the polymer formed.

4. The process of claim 1 wherein oxygen is excluded from the reaction mass.

5. Process of claim 1 wherein an azeotrope former is present in the reaction mass and water formed during the reactions is removed as an azeotrope with said azeotrope former such that substantially anhydrous conditions are maintained.

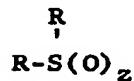
6. Process of claim 1 wherein said dihydric phenol and said alkali metal carbonate react to form the alkali metal mono-salt thereof, reacting said mono-salt with said dihalobzenoid compound to form a compound joined by an aromatic ether linkage and having a hydroxyl group and a halogen group, reacting the hydroxyl group of said compound with said alkali metal carbonate to form the alkali metal salt thereof, and reacting the alkali metal salt of said compound with said dihalobzenoid compound.

7. Process of claim 1 wherein said alkali metal bicarbonate decomposes into the alkali metal carbonate which then reacts with aromatic hydroxyl groups present in the reaction mass.

8. Process of claim 1 wherein said dihydric phenol is 4,4'-dihydroxydiphenyl sulfone and said dihalobzenoid compound is 4,4'-dihalodiphenyl sulfone, wherein from one to 10 per cent in excess of one mole of alkali metal carbonate is employed for each mole of 4,4'-dihydroxydiphenyl sulfone, and wherein the alkali metal bicarbonate formed decomposes into the alkali metal carbonate which then reacts with aromatic hydroxyl groups present in the reaction mass.

9. Process for preparing substantially linear thermoplastic polyarylene polyethers which comprises simultaneously contacting under substantially anhydrous conditions, a halophenol having an inert electron withdrawing group in at least one of the positions ortho or para to the halogen atom

with at least one-half mole of alkali metal carbonate per mole of halophenol in the liquid phase of an organic reaction solvent having the formula



where each R represents a member of the group consisting of monovalent lower hydrocarbon groups free of aliphatic unsaturation on the alpha carbon atoms and, when connected together, represents a divalent alkylene group, and z is an integer from 1 to 2 inclusive, reacting said halophenol with said alkali metal carbonate to form the alkali metal salt thereof and the bicarbonate of said alkali metal, and reacting the thus formed alkali metal salt with itself in the liquid phase of said reaction solvent.

10. Process of claim 9 wherein said halophenol is p-(p-chlorophenylsulfonyl)phenol, wherein from one-half to 10 per cent in excess of one-half mole of alkali metal carbonate is employed for each mole of halophenol and wherein the alkali metal bicarbonate formed decomposes into the alkali metal carbonate which then reacts with aromatic hydroxyl groups present in the reaction mass.



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